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(54) **LITHIUM AND POTASSIUM COPOLYSILICATE BARRIER COATINGS**

SCHUTZBESCHICHTUNGEN AUS LITHIUM- UND KALIUMKOPOLYSILIKATES

REVETEMENTS D'ISOLATION A BASE DE COPOLYSILICATE DE POTASSIUM ET DE LITHIUM

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EP 0 900 250 B2

DescriptionField of the Invention

5 **[0001]** The present invention relates generally to silicate-based barrier coatings for polymeric film or sheet.

Background of the Invention

10 **[0002]** Alkali metal polysilicates have long been known as protective coatings that modify the permeability or surface characteristics of polymeric films and other articles. Lithium (Li), sodium (Na), and potassium (K) polysilicates are known to be effective as protective coatings for a variety of surfaces. For example, Japanese Patent Publication No. H7-18202, published January 20, 1995 refers to a water-insoluble, coating material and binder for use on metals, synthetic resins, glass, wood, cement, etc, which contains mixtures of an aqueous solution of sodium or potassium silicate and an aqueous solution of lithium silicate, where the ratio of the sodium or potassium silicate to lithium silicate is in the range of 1-3.

15 **[0003]** As another example, Hecht and Iler, Canadian Patent No. 993,738, describe a gas and liquid-impermeable coating for polymeric substrates comprising lithium polysilicate having a mole ratio of SiO_2 to Li_2O of about 1.6 to 4.6. However, polymeric articles are known to become hazy after certain polysilicate coatings have been incorporated. The tendency of sodium (Na) polysilicate coatings to effloresce, i.e., to become covered by powdery crystalline material as a result of atmospheric exposure, has been documented [Weldes and Lange, Ind. Engin. Chem., 61(4):28-44 (1969)]. This characteristic has similarly been observed for lithium polysilicate coatings by the present inventors. In contrast, pure potassium polysilicate coatings do not effloresce, but suffer severe loss of barrier performance above 50% relative humidity (RH). Pure lithium polysilicate coatings, on the other hand, exhibit little or no loss of barrier performance over the same relative humidity range.

20 **[0004]** There remains a need in the art of barrier coatings for coating compositions and methods which overcome the above deficiencies, and are widely available as vapor, gas and/or aroma barriers for polymeric articles, e.g., packaging products.

Summary of the Invention

30 **[0005]** In one aspect, the present invention provides a method for providing improved vapor, gas and aroma barrier properties at high relative humidities to a polymeric film or sheet. The method involves coating the film or sheet with a barrier coating solution containing a lithium-potassium copolysilicate of the formula $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ wherein x is the mole fraction of Li_2O in the combined alkali metal oxides (M_2O), and y is the $\text{SiO}_2:\text{M}_2\text{O}$ mole ratio. In this method x is between > 0 and 0,5 and y has a value greater than 4,6 up to 10 or x ranges from 0,5 to less than 1 and y ranges from 1 up to 10.

35 **[0006]** In another aspect, the present invention provides a novel vapor, gas and/or aroma barrier coating solution for polymeric film or sheet comprising a copolysilicate of the above formula, which overcomes deficiencies in the art. The aforementioned coating solution is represented by the general formula above, except that x ranges from 0,5 to less than 1 and y is between 4,6 and 10. The coating solution is preferably colorless or transparent and can contain a suitable surfactant.

40 **[0007]** Another aspect of this invention provides a polymeric film or sheet coated with the above described barrier coating solution. The article may be typically a polymer film, such as those employed in the packaging of food-stuffs, or a sheet.

45 **[0008]** Other aspects and advantages of the present invention are described in the detailed description below and in the claims.

Brief Description of the Drawings

50 **[0009]** Fig. 1 is a graph of the hazing rate (in absolute percentage per day, i.e., a value of one indicates an increase of, for example, from 5% to 6% haze in a single day) vs. the mole fraction x of Li_2O in the copolysilicate $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$. This figure depicts the dependence of the hazing rate on the amount of lithium in the coating composition.

Detailed Description of the Invention

55 **[0010]** The present invention overcomes the deficiencies in prior art vapor barrier coatings. This invention includes a method for providing improved vapor, gas, and/or aroma barrier properties at high relative humidities to polymeric film or sheet using coating solutions containing a lithium-potassium co-polysilicate. The invention also provides novel

coating solutions for the film or sheet. The coating solutions used in the present method provide excellent vapor, gas and aroma barrier characteristics at high relative humidity in comparison with pure potassium polysilicates, and exhibit markedly reduced rates of efflorescence in comparison with pure lithium polysilicates.

I. Definitions

[0011] The term "vapor" implies a liquid at partial pressure, such as water vapor. The term "gas" includes oxygen, nitrogen, carbon dioxide and others. "Aroma" includes those materials which bear a fragrance, for example, menthol and others. For simplicity, as used herein, the term "vapor barrier" can be interpreted to mean a barrier to gases and aromas as well as traditionally defined vapors.

[0012] Similarly as used herein, the term "solution" is interpreted to include colloidal dispersions and suspensions. By "colloidal dispersion or suspension" is meant any dispersion or suspension of particles in liquid, the particles being of a size greater than molecular scale that do not settle out. Generally the particle size in a suspension or dispersion of this invention are from 10 to 50,000 Angstroms.

"Coating solution" as used herein is meant a liquid containing dissolved or suspended solids that do not settle out and which is used to apply said solids to a substrate.

II. The Invention

[0013] The method of the invention specifically involves coating a polymeric film or sheet with a barrier coating solution containing a lithium and potassium copolysilicate. The coating solution contains a copolysilicate, i.e., a mixture of two different alkali metal polysilicates. More specifically, the coating solutions result from a mixture of lithium and potassium polysilicates. These coating solutions are characterized by copolysilicate of the general formula $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$, in which the mole fraction of Li_2O is x and the molar ratio of SiO_2 to M_2O is y . In the coating solutions useful in the method of the present invention, the co-polysilicate is one in which y is between 1 and 10, if x ranges from 0.5 to less than 1, or y is greater than 4.6 and up to ten if x is between > 0 and 0.5.

[0014] Certain novel coating solutions for use in the above-described method are provided by the formula above, in which x ranges from 0.5 and 1 and y ranges from a value greater than 4.6 and 10.

[0015] Coating solutions useful in the method, as well as the novel coating solutions of this invention, can also contain a suitable surfactant to reduce surface tension. Surfactants can be anionic, cationic and nonionic, and many surfactants of each type are available commercially. Preferably, the surfactant useful in the methods and solutions of this invention is nonionic. A suitable surfactant for inclusion in these compositions possesses a critical micelle concentration sufficiently low to ensure a dried coating uncompromised by residual surfactant. Most preferably, the surfactant is selected from the group consisting of acetylenic glycols (e.g., such as those provided commercially by Air Products) and alkyl ethoxylates (such as those provided commercially by Hoechst Celanese and many others). The amount of surfactant added to the coating solution or composition will depend on the particular surfactant selected, but should be the minimum amount of surfactant that is necessary to achieve wetting of the polymer film or sheet while not compromising the performance of the dried coating. For example, typical surfactant amounts can be less than or equal to 0.1% by weight of an acetylenic glycol or an alkyl ethoxylate.

[0016] A typical coating solution according to this invention is preferably colorless and transparent. A coating solution of the invention may be prepared from commercially available lithium polysilicate and potassium polysilicate solutions. For example, a commercially available colloidal suspension of lithium polysilicate may be blended with a commercially available potassium polysilicate colloidal suspension to make the coatings of the present invention. It should be noted that one can prepare the coating solutions of the invention by using the "parent" products which are used to produce the commercially available polysilicates. However, such preparation is well-known and unnecessary in view of the commercial availability of the lithium and potassium polysilicate solutions.

[0017] As illustrated in Example 1 below, one exemplary commercially available product bearing the trademark Inobond® Li 2043 (van Baerle & Cie AG) is an aqueous colloidal suspension of lithium polysilicate which contains ~24.5% by weight silicon dioxide and ~3.0% by weight lithium oxide. Another useful product bears the trademark K-4009 (van Baerle & Cie AG) and is an aqueous colloidal suspension containing ~26.8% by weight silicon dioxide and ~13% by weight potassium oxide. Such components are then mixed with water to produce a desired solids content.

[0018] The molar ratio, y , of $\text{SiO}_2:\text{M}_2\text{O}$ of the dried coatings may be determined by the molar ratios of $\text{SiO}_2:\text{Li}_2\text{O}$ and $\text{SiO}_2:\text{K}_2\text{O}$ in the starting alkali metal polysilicates. One may, however, desire to modify the overall $\text{SiO}_2:\text{M}_2\text{O}$ mole ratio in the copolysilicate coating. This may be accomplished by the addition of aqueous suspensions of colloidal silica to the coating solution. As described in Example 4, below, one exemplary commercially available product bearing the trademark Ludox® AS-30 (DuPont Specialty Chemicals) is an aqueous colloidal suspension of silicon dioxide which contains 30% by weight solids. Such colloidal dispersions are available under a variety of trademarks including Ludox® (DuPont Specialty Chemicals) and Klebosol® (Societe Francaise Hoechst).

[0019] While a typical useful solids content for coating solutions of this invention is up to 25% by weight of solids, the desired solids content depends entirely on the coating method used, and may be readily adjusted by techniques well known to the art to achieve a desired coating thickness of the dry coating on the selected film or sheet. For example, coating on a thin film or sheet are desirably between 200 to 500 nm of dry coating, and more preferably 300 nm. Such an adjustment is well within the skill of the art [see, e.g., Canadian Patent No. 993,738].

[0020] The vapor barrier coating mixtures are then subjected to a period of stirring and, optionally, filtration. Optionally, a surfactant may be added at this stage to reduce the surface tension of the coating solution. For example, the commercially available Genapok® 26-L-60N nonionic surfactant (Hoechst Celanese) or other surfactants represented by trademarks such as Genapok® UD050 [Hoechst] and Dynol 604® may be added at this stage. The vapor barrier coating solution is thus ready to be applied to a polymeric surface or substrate.

[0021] The lithium-potassium copolysilicate coatings of the invention can be used on a variety of polymeric film or sheet surfaces to improve (i.e., reduce) the permeability of the products to vapors, such as oxygen, carbon dioxide, nitrogen and others. Typical organic aromas and vapors include, but are not limited to, d-limonene, cinnamaldehyde, vanillin, menthol, gasoline and perfume fragrances. These coatings are particularly advantageous where the polymers used to prepare the film or sheet do not provide sufficient vapor, gas, or aroma impermeability for the desired application.

[0022] Suitable film or sheet to be coated with the above-described coating solutions include film or sheet formed of polymers including polyesters, such as poly(ethylene terephthalate) (PET); polyolefins, particularly polypropylene, polystyrene, polyethylene and cycloolefins (COC), such as a copolymer of ethylene and norbornene [US Patent No. 5,087,677]; and polyamides, such as nylon. Especially preferred film or sheet for coating according to this invention include polypropylene films, PET films, nylon films, films used in covering food products (e.g., meats, poultry), made of the foregoing polymers.

[0023] The polymeric film or sheet to be coated by the compositions of the invention may be previously untreated. Optionally, the polymeric film or sheet may be first plasma treated to improve wetting and adhesion by the barrier coating as described in the following Example 1. Alternatively, the polymeric film or sheet may be corona-treated by the industry-wide corona discharge treatment method. In instances where corona-treatment of the polymer does not cause suitable wetting of the coating on the polymer, a suitable primer may be first applied to the polymeric film or sheet. For example, in the case of polypropylene, a primer solution of poly(vinyl alcohol) or poly(hydroxystyrene) may be used to improve wetting of the barrier coating solutions on the polymer.

[0024] The polymer may also have been flame treated, or chemically etched and oxidized prior to the application of the coating solution of this invention.

[0025] The substrate may be a film that contains on at least one side a heat seal layer. Such heat seal layers may be made of an ethylene-propylene copolymer or ethylene-propylene-butylene terpolymer. Thus, the coating solution is applied on the surface of the heat seal layer. Alternatively, where a film contains one side coated with the heat seal layer, the coating solution of the present invention can be applied to the surface of the film opposite the surface coated with the heat seal layer. The polymeric film or sheet may also comprise a protective topcoat layer. The coatings of this invention may be applied over the topcoat layer.

[0026] The coatings of this invention may be applied to the selected polymeric film or sheet by conventional coating techniques known to those of skill in the art. These techniques include, without limitation, roll coating, spray coating, and dip coating techniques. Roll coating techniques include, but are not limited to, rod, reverse roll, forward roll, air knife, knife over roll, blade, gravure and slot die coating methods. General descriptions of these types of coating methods may be found in texts, such as Modern Coating and Drying Techniques, (E. Cohen and E. Guttoff, eds; VCH Publishers) New York (1992) and Web Processing and Converting Technology and Equipment, (D. Satas, ed; Van Nostrand Reinhold) New York (1984). The method of application is not a limitation on the present invention, but may be selected from among these and other well-known methods by the person of skill in the art.

[0027] After coating, the coated film or sheet must be dried at a selected temperature of room temperature or greater than room temperature. The selection of the drying temperature depends on the desired time for drying; that is, accelerated drying times may be achieved at elevated temperatures which would not be necessary if a longer time period for drying was acceptable. One of skill in the art can readily adjust the oven temperature and drying time as desired. The performance of the dried vapor barrier coating is insensitive to the drying temperature over the range 25-200°C. A significant advantage of the present coatings and method is that low temperature (<100°C) drying makes this process compatible with requirements of biaxially oriented polypropylene (BOPP) film processing.

[0028] The compositions and methods of this invention are further illustrated by the following examples, which are not intended to limit the scope of this invention.

EXAMPLE 1: VARIATION OF LITHIUM OXIDE MOLE FRACTION IN COPOLYSILICATE COATINGS ON BIAXIALLY ORIENTED PET FILM**A. Preparation of Coating Solutions**

[0029] A series of seven lithium-potassium copolysilicate barrier coating solutions of the invention were prepared, as indicated in Table 1. The compositions of these polysilicate coatings of the invention are expressed as the mole fraction, x , of Li_2O in the copolysilicate $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$, with values of x ranging from 0 to 1. With continuous stirring, Inobond® Li 2043 lithium polysilicate solution (van Baerle & Cie AG) having 3.0% w/w Li_2O and 24.5% w/w SiO_2 , was mixed with water. K-4009 potassium polysilicate solution (van Baerle & Cie) having 13.0% w/w K_2O and 26.85% w/w SiO_2 was added to the lithium polysilicate solution. Genapol® 26-L-60N nonionic surfactant (Hoechst Celanese), as a 1% by weight solution in water, was then added to improve wetting of the poly(ethylene terephthalate) (PET) substrates. Each coating mixture in Table 1 was stirred overnight then filtered through diatomaceous earth. The resulting coating solutions had 15% total solids and 0.01% surfactant. The $\text{SiO}_2:\text{M}_2\text{O}$ mole ratio, y , ranged from 3.24 at $x=0$ to 4.05 at $x=1.0$.

Table 1
 Recipes for Preparing a Series of Lithium-Potassium
 Copolysilicates for Barrier Coatings

Solution No.	Mass of Inobond® LI 2043 (g)	Mass of K-4009 (g)	Mass of H ₂ O (g)	Mass of 1.0% Genapol® 26-L-60N (g)	Mole Fraction x of Li ₂ O	SiO ₂ : M ₂ O mole ratio
1 Comparative	0	75.3	122.7	2.0	0.00	3.24
2 Comparative	17.7	63.0	117.3	2.0	0.17	3.38
3 Comparative	35.7	50.6	111.7	2.0	0.34	3.51
4	53.1	38.8	106.1	2.0	0.50	3.64
5	70.6	28.5	100.9	2.0	0.66	3.77
6	89.6	13.4	95.0	2.0	0.83	3.91
7 Comparative	109.1	0	88.9	2.0	1.00	4.05

B. Preparation of Coated Films

[0030] Four inch circles were cut from PET film (Hoechst Diafoil, Hostaphan® 2400, 12,5 µm thick) with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. The samples were then plasma treated to improve wetting by copolysilicate coating solutions and adhesion of dried copolysilicate coatings. Plasma treatment was performed using a Plasma Preen microwave reactor operated at 50% power with 2 Torr of oxygen. The treatment duration was 5 s. Approximately 10 g of coating solution was dispensed on the PET film before spinning at 2000 rpm for 10 s. The coated films were dried in an oven maintained at 50°C for ~30 s.

[0031] Several coated film samples were prepared with each coating solution described in Table 1. Separate samples were selected for accelerated aging/haze measurements and oxygen transmission rate (OTR) measurements as a function of relative humidity.

C. Measurement of Haze Formation

[0032] Optical haze was measured with a spectrophotometer (MacBeth Color-Eye 7000) conforming to ASTM D 1003-61. Samples were characterized shortly after spin-coating and then placed in an environmental chamber (Tenney TH Jr.) maintained at 80°C and 85% relative humidity. Samples were periodically removed from the chamber for haze measurement over a period of two weeks.

[0033] The initial linear rate of haze formation by efflorescence is calculated by least-squares fit to a plot of % haze vs. time. At longer times the % haze reaches a plateau, with the plateau value proportional to the lithium content of the copolysilicate coating. Fig. 1 depicts the dependence of the initial rate of haze development on coating composition. The hazing rate increases linearly with increasing lithium content.

D. Measurement of Oxygen Transmission Rates

[0034] The barrier performance of the coated film samples was assessed by measurement of the OTR. OTR measurements were performed using a Mocon Oxtran 2000 instrument. Table 2 presents OTR values at 30°C (OTR units: cm³/[m² atm day]) vs. relative humidity for a series of (Li₂O)_x(K₂O)_{1-x}(SiO₂)_y copolysilicate barrier coatings on 12,5 µm PET film.

Table 2

Oxygen Transmission Rates (cm ³ /[m ² day atm]) of Lithium-Potassium Copolysilicate Barrier Coatings on 12,5 µm thick PET film vs. Composition and Relative Humidity						
Mole fraction x of Li ₂ O	Relative Humidity					
	Dry	40%	60%	70%	80%	90%
0.00 Comp.	13.1	9.5	75.4	115.8	132.1	131.6
0.17 Comp.	4.5	4.5	5.9	33.1	87.2	128.4
0.34 Comp.	3.1	3.1	3.0	1.8	42.0	101.1
0.50	3.7	3.2	3.1	2.7	14.3	17.7
0.66	7.7	4.9	4.2	3.0	3.1	15.5
0.83	15.5	6.5	5.8	5.4	2.2	12.7
1.00 Comp.	14.8	8.8	7.9	7.5	5.4	13.5

[0035] Copolysilicate coatings containing little lithium ($x \leq 0.34$) suffer severe loss of barrier performance at high humidity. Copolysilicate coatings, where $0.5 \leq x \leq 1$, provide good barrier performance at high humidity on PET film while, as shown in Fig. 1, having significantly reduced susceptibility to efflorescence, as compared to a lithium polysilicate coating.

**EXAMPLE 2: VARIATION OF THE LITHIUM OXIDE MOLE FRACTION OF COPOLYSILICATE COATINGS ON
BIAXIALLY ORIENTED PET FILM****A. Preparation of solutions**

[0036] A series of three lithium-potassium copolysilicate barrier coating solutions was prepared using the following recipe and quantities listed in Table 3. As in Example 1, the value x refers to the mole fraction x of Li_2O in the copolysilicate $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$. With continuous stirring, Inobond® Li 2043 was mixed with distilled water. K-4009 potassium polysilicate solution was added with stirring to the lithium polysilicate solution. The resulting coating solutions had 10% total solids. The $\text{SiO}_2:\text{M}_2\text{O}$ mole ratio, y, ranged from 3.51 at $x=0.33$ to 3.78 at $x=0.67$. Analogous solutions containing 10% solids of the individual alkali metal polysilicates were prepared as comparative samples.

B. Preparation of coated film

[0037] Four inch circles were cut from biaxially oriented PET film (Hoechst Diafoil, Hostaphan® 2400, 12,5 μm thick), with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. The samples were then plasma treated with a Plasma Preen microwave reactor operated at 50% power and 2 Torr of oxygen. The treatment time was 5 s. Approximately 10 0g of coating solution was dispensed onto the polymer film. A spreading spin cycle of 2 s at 350 rpm was followed by a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50°C for about 30 s. Several coated film samples were prepared with each coating solution described in Table 3.

TABLE 3
Recipes For The Preparation of Lithium-Potassium Copolysilicate Barrier Coatings

Solution Number	Mole fraction x of Li_2O	$\text{SiO}_2:\text{M}_2\text{O}$ Mole Ratio	Mass of Inobond® Li 2043(g)	Mass of K-4009 (g)	Mass of Water (g)
1 Comparative	0.00	3.24	—	125.5	374.5
2 Comparative	0.33	3.51	57.8	85.6	356.6
3	0.50	3.64	88.4	64.5	347.1
4	0.67	3.78	119.6	43.0	337.5
5 Comparative	1.00	4.05	181.8	—	318.2

C. Measurement of oxygen transmission rate.

[0038] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument Table 4 presents the oxygen transmission rate results for copolysilicate coated PET film as a function of relative humidity. As a point of reference, uncoated Hostaphan® 2400 grade PET film (12,5 μm) possesses an oxygen transmission rate of approximately

170 cm³/[m² day atm] when tested at 30°C and 0% relative humidity. The OTR reduction for this example is significantly better than the data in Example 1.

TABLE 4

Oxygen Transmission Rates of Lithium-Potassium Copolysilicate Barrier Coatings on 12,5 µm thick PET film vs. Composition and Relative Humidity		
Mole fraction x of Li ₂ O	Relative Humidity (%)	O ₂ Transmission Rate (cm ³ /[m ² day atm] at 30°C)
Comp. 0.00	0	3.72
Comp. 1.00	0	0.41
Comp. 0.00	90	126
Comp. 1.00	90	2.75
Comp. 0.00	60	38
Comp. 1.00	30	0.43
Comp. 0.33	0	1.29
0.67	0	0.11
0.50	45	1.04
0.50	45	0.02

EXAMPLE 3: VARIATION OF LITHIUM OXIDE MOLE FRACTION IN COPOLYSILICATE COATINGS ON BIAXIALLY ORIENTED POLYPROPYLENE FILM

A. Preparation of Solutions

[0039] A series of three lithium-potassium copolysilicate barrier coating solutions were prepared as described in Example 2. Analogous solutions containing 10% solids of the individual alkali metal polysilicates were prepared as comparative samples. Additionally a priming solution consisting of poly(p-hydroxystyrene) in aqueous base was prepared by adding in order, with stirring, 4.19 g of lithium hydroxide monohydrate and 1.00 g polymer grade poly(p-hydroxystyrene) in sufficient distilled water to make 100.0 ml of solution. The resulting solution contained 1% by weight poly(p-hydroxystyrene) in 0.1 N aqueous lithium hydroxide.

B. Preparation of coated film

[0040] Four inch circles were cut from biaxially oriented polypropylene film (Trespaphan® FND 30, 30 µm thick) with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. The samples were then plasma treated with a Plasma Preen microwave reactor operated at 50% power and 2 Torr of oxygen. The treatment time was 5 s. Approximately 10 g of poly(p-hydroxystyrene) primer solution was dispensed onto the polymer film. A spreading spin cycle of 2 s at 350 rpm was followed by a spin cycle of 10 s at 2000 rpm. The primed films were dried in an oven maintained at 50°C for about 30 s. Subsequently, approximately 10 g of lithium-potassium copolysilicate barrier coating solution was dispensed onto the primed polymer film. A spreading spin cycle of 2 s at 350 rpm was followed by a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50°C for about 30 s.

[0041] Several coated film samples were prepared with each coating solution described in Table 3. As comparative samples, films were also prepared in which the copolysilicate coating step was omitted.

C. Measurement of oxygen transmission rates

[0042] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument Table 5 presents the oxygen transmission rate results for copolysilicate barrier coated biaxially oriented polypropylene film (30 µm thick) as a function of relative humidity. As a point of reference, uncoated FND 30 grade polypropylene possesses an oxygen transmission rate of approximately 1700 cm³/[m² day atm] when tested at 30°C and 0% relative humidity, essentially the same as the value obtained for primed but uncoated film as shown in Table 5.

TABLE 5

Oxygen Transmission Rates of Lithium-Potassium Copolysilicate Barrier Coatings on 30 μm thick BOPP film vs. Composition and Relative Humidity		
Mole fraction x of Li_2O	Relative Humidity (%)	O_2 Transmission Rate ($\text{cm}^3/[\text{m}^2 \text{ day atm}]$ at 30°C)
Comp. 0.00	0	401
Comp. 1.00	90	44
Comp. 0.00	90	1597
Comp. 1.00	30	711
Comp. 0.00	60	157
Comp. 1.00	0	1217
0.67	0	1190
Comp. 0.33	90	400
0.50	45	45
Comp. Primed film with no copolysilicate coating	0	1661

EXAMPLE 4: VARIATION OF SILICA:METAL OXIDE MOLE RATIO IN COPOLYSILICATE COATINGS CONTAINING EQUIMOLAR AMOUNTS OF LITHIUM AND POTASSIUM OXIDES

[0043] Example 1 demonstrates that the rate of haze formation by efflorescence in lithium polysilicate barrier coatings can be reduced by adding potassium silicate. Addition of potassium silicate, however, compromises the excellent oxygen barrier performance of lithium silicate coatings at high humidity. A balance of low efflorescence rate and satisfactory barrier performance at high humidity is achieved with approximately equimolar lithium-potassium copolysilicate blends.

[0044] A copolysilicate barrier coating with a lithium:potassium mole ratio of one produced from K-4009 ($\text{SiO}_2:\text{K}_2\text{O} = 3.24$) and Li 2043 ($\text{SiO}_2:\text{Li}_2\text{O} = 4.06$), has a $\text{SiO}_2:\text{M}_2\text{O}$ mole ratio, y, of 3.64. In this experiment, y was increased by either: (1) using a potassium polysilicate solution with a higher $\text{SiO}_2:\text{K}_2\text{O}$ mole ratio or (2) adding colloidal silica. The first approach permits y of the present copolysilicate coatings to be increased from 3.64 to 4.0. The upper limit of y is dictated by the $\text{SiO}_2:\text{K}_2\text{O}$ mole ratio of commercially available potassium polysilicate coating solutions. The second approach, adding colloidal SiO_2 , permits solutions of even higher y value to be prepared.

A. Preparation of coating solutions

[0045] In this example, the source of lithium polysilicate was Inobond® Li 2043. The source of potassium polysilicate was either K-4009 or KASIL® #1 potassium polysilicate solution (PQ Corporation) having 8.30% w/w K_2O and 20.8 % w/w SiO_2 . The colloidal silica source was chosen from the list of Ludox® colloidal silica suspensions (DuPont Specialty Chemicals) described in Table 6. Dupont's Ludox® CL-X silica is encapsulated in Al_2O_3 . Equivalent products marketed under the tradename Klebasol®, are available from Societe Francaise Hoechst.

TABLE 6

Description of Dupont Specialty Chemicals Ludox® Brand Colloidal Silicas			
Colloidal Silica Grade	Counterion	% Solids	Particle Size (nm)
Ludox® HS-40	sodium	40.0	12
Ludox® AS-30	ammonium	30.0	22
Ludox® CL-X	sodium (Al_2O_3)	45.0	22

[0046] A series of lithium-potassium copolysilicate barrier coating solutions with a Li_2O mole fraction of $x=0.5$ and differing $\text{SiO}_2:\text{M}_2\text{O}$ mole ratios, y, was prepared according to the amounts listed in Table 7. In one experiment a potassium silicate solution, KASIL® #1, having a $\text{SiO}_2:\text{K}_2\text{O}$ mole ratio of 4 was used. With continuous stirring, distilled water, potassium polysilicate solution, lithium polysilicate solution, and Ludox® colloidal silica were combined in the

order given. The resulting coating solutions had 10% total solids and had $\text{SiO}_2:\text{M}_2\text{O}$ mole ratios, y , between 3.64 and 10.0. Analogous solutions containing 10% solids of the alkali metal polysilicates and no additional colloidal silica were prepared as comparative samples.

TABLE 7
Recipes For The Preparation of Lithium-Potassium Copolysilicate
Barrier Coatings Having Various $\text{SiO}_2:\text{M}_2\text{O}$ Mole Ratios, y and
An Equimolar Ratio of Lithium to Potassium Oxides

$\text{SiO}_2:\text{M}_2\text{O}$ Mole Ratio (y)	Source of Colloidal Silica (Ludox®)	Mass of Colloidal Silica (g)	Source of Potassium Polysilicate	Mass of Potassium Polysilicate (g)	Mass of Inobond® Li 2043 (g)	Mass of Distilled Water (g)
3.64	None	-	K-4009	12.89	7.66	69.37
3.99	None	-	KASIL® #1	18.84	16.50	64.74
3.99	HS-40	1.73	K-4009	12.02	16.50	69.79
5.00	HS-40	5.60	K-4009	10.00	13.68	70.63
5.00	AS-30	7.47	K-4009	10.00	13.70	68.80
5.00	CL-X	4.98	K-4009	10.01	13.73	71.30
7.00	HS-40	10.44	K-4009	7.52	10.34	71.75
7.00	AS-30	13.90	K-4009	7.49	10.28	68.22
7.00	CL-X	9.27	K-4009	7.52	10.31	72.91
10.00	HS-40	14.45	K-4009	5.45	7.50	72.64

B. Preparation of coated film samples

[0047] Four inch circles were cut from biaxially oriented PET film (Hoechst Diafoil, Hostaphan® 2400, 12,5 µm thick) with a scalpel. Any dust on the film was blown off with a jet of clean filtered air. The film samples were then plasma treated to improve wetting by barrier coating solutions and adhesion of dried barrier coatings. Plasma treatment was performed using a Plasma Preen microwave reactor operated at 50% power with 2 Torr of oxygen. The treatment duration was about 7 s.

[0048] Approximately 10 g of coating solution was dispensed onto the polymer film. A spreading spin cycle of 2 s at 350 rpm was followed by a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50°C for about 30 s.

C. Oxygen barrier performance

[0049] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument. Samples were tested at 23°C and 50% relative humidity. Table 8 presents oxygen transmission rates as a function of SiO₂:M₂O mole ratio, y, for a series of lithium-potassium copolysilicate barrier coatings with a lithium oxide mole fraction in (Li₂O)_x(K₂O)_{1-x}(SiO₂)_y, x = 0.5. As a point of reference, uncoated 0.5 mil thick PET film has an OTR of ~115 cm³/(m² day atm) at 23°C and 50% relative humidity. These results demonstrate that good barrier performance can be achieved in copolysilicate barrier coatings with SiO₂:M₂O mole ratios as high as 10. However, the range of SiO₂:M₂O mole ratios that yield satisfactory barrier performance depends on the identity of the colloidal silica source.

TABLE 8

Oxygen Transmission Rates of Lithium-Potassium Copolysilicate Barrier Coatings on 0.5 mil thick PET film vs. SiO ₂ :M ₂ O Ratio			
SiO ₂ :M ₂ O Mole Ratio	Source of Colloidal Silica	Source of Potassium Polysilicate	OTR(cm ³ /[m ² day atm] at 23°C and 50% relative humidity)
3.64	none	K-4009	0.83
"	"	"	0.28
3.99	None	KASIL® #1	0.34
"	"	"	0.17
3.99	HS-40	K-4009	0.52
"	"	"	0.39
5.00	HS-40	K-4009	0.35
"	"	"	0.33
5.00	AS-30	K-4009	1.06
"	"	"	0.23
5.00	CL-X	K-4009	0.23
"	"	"	0.29
7.00	HS-40	K-4009	0.93
"	"	"	0.48
7.00	AS-30	K-4009	0.65
"	"	"	0.55
7.00	CL-X	K-4009	11.80
"	"	"	12.84
10.00	HS-40	K-4009	1.89
"	"	"	1.40

EXAMPLE 5: SIMULTANEOUS VARIATION OF SiO₂:M₂O MOLE RATIO, y, AND MOLE FRACTION OF Li₂O, x, IN (Li₂O)_x(K₂O)_{1-x}(SiO₂)_y COPOLYSILICATE COATINGS ON BIAXIALY ORIENTED PET FILM

A. Preparation of coating solutions

[0050] A series of lithium-potassium copolysilicate barrier coating solutions were prepared according to the amounts

listed in Table 9. With continuous stirring, distilled water, K-4009 potassium polysilicate solution, Inobond® Li 2043 lithium polysilicate solution, and Ludox® AS-30 colloidal suspension of silicon dioxide containing 30% solids (DuPont Specialty Chemicals) were combined in the order given. The resulting coating solutions had 10% total solids and had $\text{SiO}_2:\text{M}_2\text{O}$ mole ratios, y values of between 3.51 and 13. Analogous solutions containing 10% solids of the individual alkali metal polysilicates were prepared as comparative samples.

TABLE 9
Recipes for the Preparation of Lithium-Potassium Copolysilicate
Barrier Coatings Having Various $\text{SiO}_2:\text{M}_2\text{O}$ Mole Ratios and Li_2O Mole Fractions

Solution	Mole fraction of Li_2O x	$\text{SiO}_2:\text{M}_2\text{O}$ Mole ratio y	Mass of K4009 (g)	Mass of Inobond® Li 2043 (g)	Mass of Ludox® AS-30 (g)	Mass of Distilled Water (g)
1 Comp.	0.00	4.05	42.94	0.00	9.63	147.43
2 Comp.	0.00	7.67	26.12	0.00	1.97	141.91
3 Comp.	0.00	15.0	14.57	0.00	47.31	138.12
4 Comp.	0.33	4.05	30.57	20.95	6.85	141.62
5	0.50	9.5	11.46	15.71	37.05	135.79
6	0.50	9.5	11.46	15.71	37.05	135.79
7	0.50	15	7.53	10.32	47.21	134.95
8	0.67	4.05	16.40	44.96	3.68	134.97
9 Comp.	1.00	4.05	0.00	72.73	0.00	127.27
10 Comp.	1.00	11.33	0.00	27.98	41.02	131.00
11 Comp.	1.00	15.0	0.00	21.35	47.09	131.55

B. Preparation of coated film samples

[0051] Four inch circles were cut from biaxially oriented PET film (Hoechst Diafoil, Hostaphan® 2400, 12,5 µm thick), with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. The samples were then plasma treated with a Plasma Preen microwave reactor operated at 50% power and 2 Torr of oxygen. The treatment time was 5 s. Approximately 10g of coating solution was dispensed onto the polymer film. A spreading spin cycle of 2 s at 50 rpm was followed by a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50°C for about 30 s. Several coated film samples were prepared with each coating solution described in Table 9.

C. Measurement of oxygen transmission rates

[0052] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument Table 10 presents the oxygen transmission rate results for biaxially oriented PET film (12,5 µm thick) coated with copolysilicate barrier layers having various SiO₂:M₂O mole ratios, y, and Li₂O mole fractions, x, in (Li₂O)_x(K₂O)_{1-x}(SiO₂)_y as a function of relative humidity. As a point of reference, uncoated Hostaphan® 2400 grade PET film (0.5 mil thick) possesses an oxygen transmission rate of approximately 115 cm³/[m² day atm] when tested at 23°C and 0% relative humidity.

Table 10

Oxygen Transmission Rates of Lithium-Potassium Copolysilicate Barrier Coatings on 12,5 µm thick PET film vs. SiO ₂ : M ₂ O Ratio and Mole Fraction of Li ₂ O			
SiO ₂ :M ₂ O Mole Ratio y	Mole fraction of Li ₂ O x	Relative Humidity (%)	OTR (cm ³ /[m ² day atm] at 23°C)
15.0	0.00 comp.	90	93
7.67	0.00 comp.	0	30
11.3	1.00 comp.	90	68
15.0	1.00 comp.	90	91
9.5	0.50	45	46
4.05	0.00 comp.	30	9.75
4.05	1.00 comp.	60	11
7.67	0.00 comp.	90	98
15.0	0.00 comp.	0	128
4.05	0.67	0	0.7
15.0	1.00 comp.	0	125
4.05	0.33 comp.	90	80
4.05	0.67	90	24
11.3	1.00 comp.	0	56
15.0	0.50	45	107
4.05	1.00 comp.	30	0.39
4.05	0.33 comp.	0	2.15
4.05	0.00 comp.	60	4.38

EXAMPLE 6: ROLL COATING OF LITHIUM-POTASSIUM COPOLYSILICATE BARRIER COATING ONTO BIAXIALY ORIENTED PET FILM

A. Preparation of Coating Solutions

[0053] With continuous stirring, 4,513 g KASIL® #1 potassium polysilicate solution (PQ Corporation) having 8.30% w/w K₂O and 20.8% w/w SiO₂ was mixed with 11,535 g distilled water. To the stirring potassium polysilicate solution was added 3,951 g Inobond® Li-2043 lithium polysilicate solution. The resulting coating solution had a total solids level of 12%. The values of x and y in (Li₂O)_x(K₂O)_{1-x}(SiO₂)_y were 0.5 and 4.0, respectively.

B. Preparation of Coated Films

[0054] Biaxially oriented PET film (Hoechst Diafoil, Hostaphan® 2400, 12,5 µm thick), was coated with the copoly-silicate solution described above using roll coating at a speed of 200 fpm. Corona discharge treatment was used to

increase the surface energy of the film surface immediately prior to application of the coating. Application of the coating was achieved with the use of a gravure cylinder in a reverse gravure configuration with a hard rubber backing roll. The ceramic-coated gravure cylinder possessed a laser engraved cell pattern with 220 lines per inch arranged at a 60 degree angle to the roll axis and a theoretical cell volume of 10 billion cubic micrometers per square inch.

C. Measurement of Oxygen Transmission Rate

[0055] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument. The average oxygen transmission rate obtained for 12 representative samples selected from the coated film was $0.77 \pm 0.38 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ at 23°C and 50% relative humidity. As a point of reference, uncoated 12,5 µm Hostaphan® 2400 grade PET film possesses an oxygen transmission rate of approximately $115 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ when tested at 23°C and 50% relative humidity.

EXAMPLE 7: COPOLYSILICATE COATED THICK PET FILM

A. Preparation of coating solutions

[0056] A lithium-potassium copolysilicate barrier coating solution having values of x and y in $\text{Li}_2\text{O}_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$ of 0.5 and 3.64, respectively, was prepared by adding, with continuous stirring, 176.8 g of Inobond® Li 2043 lithium polysilicate and 129.0 g of K-4009 potassium polysilicate to 694.2 g of distilled water.

B. Preparation of coated film samples

[0057] Four inch circles were cut from biaxially oriented PET film (Hoechst Diafoil, Hostaphan® 4000, 162,5 µm thick) with a circular punch and scissors. Dust on the film was blown off with a jet of clean, filtered air. The film samples were then corona treated to improve wetting by barrier coating solutions and adhesion of dried barrier coatings. Corona treatment was performed using a Tantec Lab System II with hand-held ceramic roller electrode. The treatment duration was about 20 s. Spin coating of the films was accomplished by dispensing approximately 10 g of coating solution onto the polymer film. A spreading spin cycle of 2 s at 350 rpm was followed by a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50 °C for about 30 s.

C. Measurement of oxygen transmission rate

[0058] Oxygen transmission rates were measured using a Mocon Oxtran 2000 instrument. Samples were tested at 23°C and either 0 or 48% relative humidity. Table 11 presents oxygen transmission rate results for thick biaxially oriented poly(ethylene terephthalate) film 162,5 µm thick) uncoated or coated with copolysilicate barrier layers. Note that the OTR of uncoated PET film is inversely dependent on film thickness $\sim 8 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ for 6.5 mil film vs. $\sim 115 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ for 0.5 mil film at 23°C (see Example 5). In contrast, the oxygen transmission rate of copolysilicate-coated biaxially oriented PET film is independent of substrate thickness. Thus the relative barrier improvement achievable for thick substrates is less than for thin substrates.

TABLE 11

Oxygen Transmission Rates of Lithium-Potassium Copolysilicate Barrier Coatings on 6.5 mil PET Film		
Sample	Relative Humidity (%)	O ₂ transmission rate (cm ³ /[m ² day atm] at 23°C)
Uncoated	0	7.25
"	0	8.06
"	0	7.72
Average	0	7.68±0.33
Coated	0	0.54
"	48	0.40
"	48	0.22
Average	48	0.31±0.09

EXAMPLE 8: CARBON DIOXIDE BARRIER PERFORMANCE OF COPOLYSILICATE COATED BIAXIALLY ORIENTED PET FILMS

[0059] Samples of the lithium:potassium copolysilicate coated biaxially oriented poly(ethylene terephthalate) film described in Example 6 were tested for carbon dioxide permeability. The average carbon dioxide transmission rate obtained for 4 representative samples selected from the coated film was $16 \pm 11 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ at 23°C and 0% relative humidity. As a point of reference, uncoated 12,5 μm Hostaphan® 2400 grade poly(ethylene terephthalate) film possesses a carbon dioxide transmission rate of approximately $440 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ when tested at 23°C and 0% relative humidity.

EXAMPLE 9: AROMA BARRIER PERFORMANCE OF COPOLYSILICATE-COATED, BIAXIALLY-ORIENTED POLYPROPYLENE FILM**A. Preparation of Coating Solution**

[0060] A lithium-potassium copolysilicate barrier coating solution having values of x and y of 0.5 and 3.64 for $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$, respectively, was prepared using inobond® Li 2043 lithium polysilicate, K-4009 potassium polysilicate, and water using the method described in Example 1. The resulting solution had a total solids level of 12% by weight

B. Preparation of Coated Film Sample

[0061] Biaxially-oriented polypropylene film (Trespaphan® FND 20, 20 μm thick) was corona treated, then primed with a poly(vinyl alcohol) solution by reverse gravure coating. The primed film was coated with the copolysilicate solution described in this example using roll coating at a speed of 200 fpm. Application of the coating was achieved with the use of a gravure cylinder in a reverse gravure configuration with a hard rubber backing roll. The ceramic-coated gravure cylinder possessed a laser-engraved cell pattern with 220 lines per inch arranged at a 60° angle relative to the roll axis and a theoretical cell volume of 10 billion cubic micrometer per square inch.

C. Measurement of Aroma Barrier

[0062] Aroma barrier performance was tested using cinnamaldehyde as a permeant. The cinnamaldehyde transmission rates of uncoated and copolysilicate-coated film (measured with liquid cinnamaldehyde in contact with the uncoated side of the film) are $0.095 \text{ g}/(\text{m}^2 \text{ day})$ and $0.022 \text{ g}/(\text{m}^2 \text{ day})$ at 23°C , respectively.

EXAMPLE 10: COPOLYSILICATE COATED CYCLOOLEFINIC COPOLYMER FILM**A. Preparation of solutions**

[0063] A lithium-potassium copolysilicate barrier coating solution having values of x and y of 0.5 and 3.64 respectively, for $(\text{Li}_2\text{O})_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_y$, was prepared using Inobond® Li 2043 lithium polysilicate, K-4009 potassium polysilicate, and water using the method described in Example 1. The resulting solution had a total solids level of 10% by weight.

B. Preparation of coated film

[0064] Four inch circles were cut from a corona-treated, biaxially oriented film of cycloolefinic copolymer, a copolymer of ethylene and norbornene, 20 μm thick, with a scalpel. Any dust on the film was blown off with a jet of clean, filtered air. Approximately 10 g of coating solution was dispensed onto the polymer film and subjected to a spin cycle of 10 s at 2000 rpm. The coated films were dried in an oven maintained at 50°C for about 30 s.

C. Measurement of oxygen transmission rate.

[0065] Oxygen transmission rates were measured using a Mocon Oxtran 20000 instrument at 30°C and 0% relative humidity. The polysilicate coated film exhibited an OTR of $28 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ whereas an uncoated film exhibited an OTR of $2819 \text{ cm}^3/[\text{m}^2 \text{ day atm}]$ under the same conditions.

[0066] Application of the method of this invention, and utilizing the improved coating compositions of the present invention result in a much less severe loss of barrier performance at high humidities than pure potassium polysilicates and develop haze at about half (when $x \sim 0.5$) the rate of pure lithium polysilicates. More specifically, the lithium-potassium copolysilicate coatings of the present invention reduce the rate of efflorescence of pure lithium polysilicates without sacrificing the barrier qualities of such lithium-polysilicate coatings. The present invention lithium-potassium polysilicate coatings provide superior barrier properties with reduced negative side-effects caused by efflorescence.

[0067] All references and patents cited above are incorporated herein by reference. Numerous modifications and variations of the present invention are included in the above-identified specification and are expected to be obvious to one of skill in the art. Such modifications and alterations to the compositions and processes of the present invention are believed to be encompassed in the scope of the claims appended hereto.

Claims

1. A polymeric film or sheet having a lithium-potassium copolysilicate coating layer, said layer comprising a copoly-silicate of the formula $(M_2O)(SiO_2)_y$, wherein (M_2O) is $(Li_2O)_x(K_2O)_{1-x}$ and wherein
 - (i) x is between > 0 and 0.5 and y has a value of greater than 4.6 and up to 10 or
 - (ii) x ranges from 0.5 to less than 1 and y ranges from 1 up to 10
2. The article according to claim 1 wherein x ranges from 0.5 to less than 1 and y is between 4.6 and 10 .
3. The article according to claim 1 or claim 2 wherein said polymer is selected from the group consisting of a polyester, a polyolefin, a polystyrene, and a polyamide.
4. The article according to claim 3 wherein said polyolefin is selected from polyethylene, polypropylene, a cycloolefinic copolymer, and copolymers thereof.
5. The article according to claim 3 wherein said polyester is poly(ethylene terephthalate).
6. The article according to claim 5 wherein said cycloolefinic copolymer is a copolymer of ethylene and norbornene.
7. The article according to claim 4 wherein said polyamide is nylon.
8. The article according to claim 7 wherein said substrate is a film that contains on at least one side a heat seal layer.
9. The article according to claim 9 wherein said heat seal layer is made of an ethylene-propylene copolymer or ethylene-propylene-butylene terpolymer.
10. The article according to claim 1 or claim 2 wherein said substrate is plasma treated, corona treated, flame treated or chemically etched/oxidized.
11. The article according to claim 1 or claim 2 further comprising a protective topcoat layer.
12. A barrier coating solution for polymeric substrates comprising a lithium-potassium copolysilicate of the formula $(M_2O)(SiO_2)_y$, wherein M_2O is $(Li_2O)_x(K_2O)_{1-x}$, and wherein (ii) x ranges from 0.5 to less than 1 and y ranges from a value greater than 4.6 to 10 .
13. The coating solution according to claim 12, further comprising a suitable surfactant.
14. The coating solution according to claim 12, wherein the surfactant is nonionic.
15. The coating solution according to claim 14 wherein the surfactant is selected from the group consisting of acetylenic glycols and alkyl ethoxylates.
16. A method for providing barrier properties to a polymeric film or sheet, comprising coating said film or sheet with a barrier coating solution which comprises a lithium-potassium copolysilicate of the formula $(M_2O)(SiO_2)_y$ wherein M_2O is $(Li_2O)_x(K_2O)_{1-x}$ and wherein x and y are as defined in claim 1.
17. The method according to claim 16 wherein x ranges from 0.5 to less than 1 and y is between 4.6 and 10 .
18. The method according to claim 16 wherein said polymer is selected from the group consisting of a polyester, a polyolefin, a polystyrene, and a polyamide.

19. The method according to claim 18 wherein said polyolefin is selected from polyethylene, polypropylene, a cycloolefinic copolymer, and copolymers thereof.
20. The method according to claim 18 wherein said polyester is poly(ethylene terephthalate).
21. The method according to claim 19 wherein said cycloolefinic copolymer is a copolymer of ethylene and norbornene.
22. The method according to claim 18 wherein said polyamide is nylon.
23. The method according to claim 16 wherein said film contains on at least one side a heat seal layer.
24. The method according to claim 23 wherein said heat seal layer is made of an ethylene-propylene copolymer or ethylene-propylene-butylene terpolymer.
25. The method according to claim 16 wherein said film or sheet is plasma treated, corona treated, flame treated or chemically etched/oxidized prior to application of said coating.
26. The method according to claim 16 wherein said film or sheet further comprises a protective topcoat layer.
27. The film or sheet according to claim 1 having a suitable primer applied to the polymeric film or sheet.
28. The film or sheet according to claim 1 wherein the film or sheet made from polypropylene having applied a primer solution of polyvinyl alcohol.
29. The film or sheet according to claim 1 wherein the film or sheet is made from polypropylene having applied a primer solution of poly(hydroxystyrene).

Patentansprüche

1. Polymere Folie oder Bahn mit einer Lithium-Kalium-Copolysilicat-Beschichtung, wobei die genannte Beschichtung ein Copolysilicat mit der Formel $(M_2O)(SiO_2)_y$ enthält, wobei M_2O für $(Li_2O)_x(K_2O)_{1-x}$ steht und wobei
 - (i) x zwischen >0 und 0,5 liegt und y >4,6 bis 10 ist, oder
 - (ii) x 0,5 bis <1 und y 1 bis 10 ist.
2. Produkt gemäß Anspruch 1, wobei x 0,5 bis <1 ist und y zwischen 4,6 und 10 liegt.
3. Produkt gemäß Anspruch 1 oder 2, wobei das genannte Polymer aus einer Gruppe gewählt wird, die aus einem Polyester, einem Polyolefin, einem Polystyrol und einem Polyamid besteht.
4. Produkt gemäß Anspruch 3, wobei das genannte Polyolefin aus Polyethylen, Polypropylen, einem Cycloolefincopolymer und deren Copolymeren gewählt wird.
5. Produkt gemäß Anspruch 3, wobei der genannte Polyester Polyethylenterephthalat ist.
6. Produkt gemäß Anspruch 5, wobei das genannte Cycloolefincopolymer ein Copolymer von Ethylen und Norbornen ist.
7. Produkt gemäß Anspruch 4, wobei das genannte Polyamid Nylon ist.
8. Produkt gemäß Anspruch 7, wobei der genannte Träger eine Folie ist, die zumindest auf einer Seite eine Heißsiegelschicht besitzt.
9. Produkt gemäß Anspruch 8 wobei die genannte Heißsiegelschicht aus einem Ethylen-Propylen-Copolymer oder einem Ethylen-Propylen-Butylen-Terpolymer besteht.

10. Produkt gemäß Anspruch 1 oder 2, wobei der genannte Träger einer Plasmabehandlung, Coronabehandlung, Beflammung oder einer chemischen Ätzung/Oxidation unterzogen wird.
11. Produkt gemäß Anspruch 1 oder 2, das zusätzlich eine obere Schutzschicht besitzt.
- 5 12. Sperrschichtlösung für polymere Träger, umfassend ein Lithium-Kalium-Copolysilicat mit der Formel $(M_2O)(SiO_2)_y$, wobei M_2O für $(Li_2O)_x(K_2O)_{1-x}$ steht und wobei (ii) x 0,5 bis <1 und y >4,6 bis 10 ist.
- 10 13. Beschichtungslösung gemäß Anspruch 12, die zusätzlich ein geeignetes Tensid enthält.
14. Beschichtungslösung gemäß Anspruch 12, wobei das Tensid nichtionisch ist.
- 15 15. Beschichtungslösung gemäß Anspruch 14, wobei das Tensid aus einer Gruppe gewählt wird, die aus Acetylen-glycolen und Alkylethoxylaten besteht.
16. Verfahren, mit dem einer polymeren Folie oder Bahn Barriereigenschaften verliehen werden, wobei die genannte Folie oder Bahn mit einer Sperrschichtlösung beschichtet wird, die ein Lithium-Kalium-Copolysilicat mit der Formel $(M_2O)(SiO_2)_y$ enthält, wobei M_2O für $(Li_2O)_x(K_2O)_{1-x}$ steht und wobei x und y den Definitionen in Anspruch 1 entsprechen.
- 20 17. Verfahren gemäß Anspruch 16, wobei x 0,5 bis <1 ist und y zwischen 4,6 und 10 liegt.
18. Verfahren gemäß Anspruch 16, wobei das genannte Polymer aus einer Gruppe gewählt wird, die aus einem Polyester, einem Polyolefin, einem Polystyrol und einem Polyamid besteht.
- 25 19. Verfahren gemäß Anspruch 18, wobei das genannte Polyolefin aus Polyethylen, Polypropylen, einem Cycloolefincopolymer und deren Copolymeren gewählt wird.
- 30 20. Verfahren gemäß Anspruch 18, wobei der genannte Polyester Polyethylenterephthalat ist.
21. Verfahren gemäß Anspruch 19, wobei das genannte Cycloolefincopolymer ein Copolymer von Ethylen und Norbornen ist.
- 35 22. Verfahren gemäß Anspruch 18, wobei das genannte Polyamid Nylon ist.
23. Verfahren gemäß Anspruch 16, wobei die genannte Folie zumindest auf einer Seite eine Heißsiegelschicht besitzt.
24. Verfahren gemäß Anspruch 23, wobei die genannte Heißsiegelschicht aus einem Ethylen-Propylen-Copolymer oder einem Ethylen-Propylen-Butylen-Terpolymer besteht.
- 40 25. Verfahren gemäß Anspruch 16, wobei die genannte Folie oder Bahn vor dem Aufbringen der genannten Beschichtung einer Plasmabehandlung, Coronabehandlung, Beflammung oder einer chemischen Ätzung/Oxidation unterzogen wird.
- 45 26. Verfahren gemäß Anspruch 16, wobei die genannte Folie oder Bahn zusätzlich eine obere Schutzschicht besitzt.
27. Folie oder Bahn gemäß Anspruch 1, bei der ein geeigneter Primer auf die polymere Folie oder Bahn aufgebracht ist.
- 50 28. Folie oder Bahn gemäß Anspruch 1, wobei die Folie oder Bahn aus Polypropylen besteht mit einer Primerlösung aus Polyvinylalkohol versehen ist.
29. Folie oder Bahn gemäß Anspruch 1, wobei die Folie oder Bahn aus Polypropylen besteht mit einer Primerlösung aus Polyhydroxystyrol versehen ist.

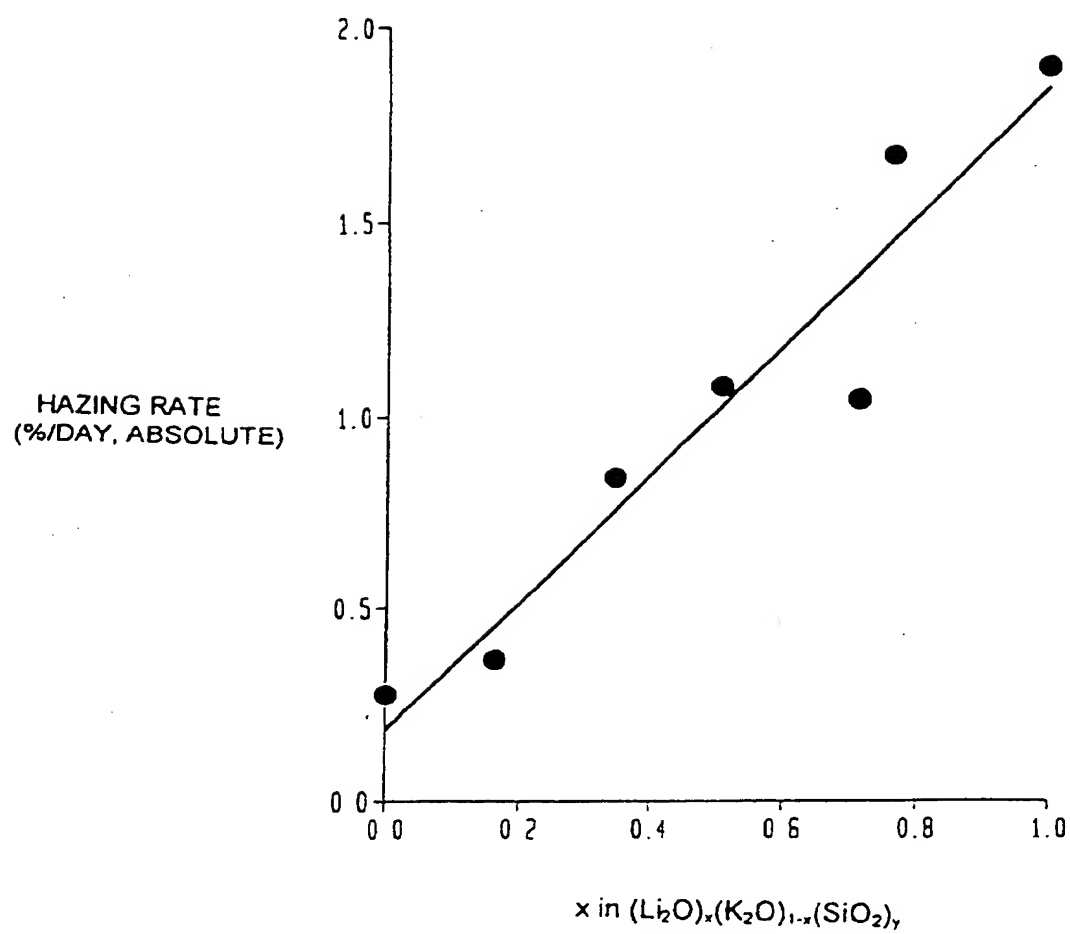
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Revendications

1. Film polymère en feuille ou en lé avec une enduction de copolysilicate de lithium-potassium, ladite enduction comprenant un copolysilicate de la formule $(M_2O)(SiO_2)_y$, M_2O étant pour $(Li_2O)_x(K_2O)_{1-x}$ et
 - (i) x étant compris entre >0 et 0,5 et y allant de >4,6 jusqu'à 10, ou
 - (ii) x étant de 0,5 jusqu'à <1 et y de 1 jusqu'à 10.
2. Produit selon la revendication 1, x allant de 0,5 jusqu'à <1 et y étant situé entre 4,6 et 10.
3. Produit selon l'une des revendications 1 ou 2, ledit polymère étant choisi dans un groupe consistant en un polyester, une polyoléfine, un polystyrène et un polyamide.
4. Produit selon la revendication 3, ladite polyoléfine étant choisie à partir de polyéthylène, de polypropylène, d'un copolymère cyclooléfinique, et de leurs copolymères.
5. Produit selon la revendication 3, ledit polyester étant un téréphtalate de polyéthylène.
6. Produit selon la revendication 5, ledit copolymère cyclooléfinique étant un copolymère d'éthylène et de norbonène.
7. Produit selon la revendication 4, ledit polyamide étant du nylon.
8. Produit selon la revendication 7, ledit support étant un film possédant au moins sur une face une couche scellable à chaud.
9. Produit selon la revendication 8 ladite couche scellable à chaud consistant en un copolymère d'éthylène-propylène ou en un terpolymère d'éthylène-propylène-butylène.
10. Produit selon l'une des revendications 1 ou 2, ledit support étant soumis à un traitement au plasma, un traitement corona, un traitement à la flamme, ou à un mordantage/oxydation chimique.
11. Produit selon l'une des revendications 1 ou 2, possédant en plus une couche de protection supérieure.
12. Solution de couche barrière pour supports polymères comprenant un copolysilicate de lithium-potassium de la formule $(M_2O)(SiO_2)_y$, M_2O étant pour $(Li_2O)_x(K_2O)_{1-x}$ et
 - (ii) x allant de 0,5 jusqu'à <1 et y de >4,6 jusqu'à 10.
13. Solution d'enduction selon la revendication 12, contenant en plus un tensioactif approprié.
14. Solution d'enduction selon la revendication 12, le tensio-actif étant non-ionique.
15. Solution d'enduction selon la revendication 14, le tensioactif étant choisi dans un groupe consistant en glycols d'acétylène et en éthoxylates d'alkyles.
16. Procédé avec lequel des propriétés barrière sont conférées à un film polymère en feuille ou en lé, ledit film en feuille ou en lé étant enduit d'une solution de couche barrière qui contient un copolysilicate de lithium-potassium de la formule $(M_2O)(SiO_2)_y$, M_2O étant pour $(Li_2O)_x(K_2O)_{1-x}$ et x et y correspondant aux définitions dans la revendication 1.
17. Procédé selon la revendication 16, x allant de 0,5 jusqu'à <1 et y étant situé entre 4,6 et 10.
18. Procédé selon la revendication 16, ledit polymère étant choisi dans un groupe consistant en un polyester, une polyoléfine, un polystyrène et un polyamide.
19. Procédé selon la revendication 18, ladite polyoléfine étant choisie à partir de polyéthylène, de polypropylène, d'un copolymère cyclooléfinique et de leurs copolymères.

20. Procédé selon la revendication 18, ledit polyester étant un téréphtalate de polyéthylène.
21. Procédé selon la revendication 19, ledit polymère cyclooléfinique étant un copolymère d'éthylène et de norbonène.
- 5 22. Procédé selon la revendication 18, ledit polyamide étant du nylon.
23. Procédé selon la revendication 16, ledit film possédant au moins sur une face une couche scellable à chaud.
24. Procédé selon la revendication 23, ladite couche thermo-scellable consistant en un copolymère d'éthylène-propylène ou en un terpolymère d'éthylène-propylène-butylène.
- 10 25. Procédé selon la revendication 16, ledit film en feuille ou en lé étant soumis avant l'application de ladite enduction à un traitement au plasma, un traitement corona, un traitement à la flamme ou à un mordantage/oxydation chimique.
- 15 26. Procédé selon la revendication 16, ledit film en feuille ou en lé possédant en plus une couche de protection supérieure.
27. Film en feuille ou en lé selon la revendication 1, un primaire approprié étant appliqué sur le film polymère en feuille ou en lé.
- 20 28. Film en feuille ou en lé selon la revendication 1, le film en feuille ou en lé consistant en polypropylène doté d'une solution de primaire en alcool polyvinylique.
- 25 29. Film en feuille ou en lé selon la revendication 1, le film en feuille ou en lé consistant en polypropylène doté d'une solution de primaire en polyhydroxystyrène

FIG. 1



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